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Wilson

Henry D.

Cost

I. ORTHO-SULPHAMINEBENZOIC ACID.

II. ORTHO-CARbamINEBENZENESULPHONIC ACID.

A Dissertation submitted to the Board of
University Studies of the Johns Hopkins Uni-
versity for the Degree of Doctor of Philosophy.

by

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I also wish to acknowledge my gratitude for instruction received from Professor Morse, Professor Clark and Dr. Mathews.

PART I.

ORTHOSULPHUMIC BENZOIC ACID.

Introduction.

Reinser and Fahlberg by oxidizing orthotoluene sulphamide with potassium ferricyanide discovered the substance known as benzoic sulphonic acid. (1) W. A. Noyes by oxidizing orthotoluene sulphamide with potassium ferricyanide discovered orthosulphamic benzoic acid. He gave to the acid the formula $C_6H_5NH_2SO_3H$. The acid is described as being easily soluble in alcohol and ether and quite readily soluble in cold water. It crystallized in two different forms under different conditions: From the barium salt, acidified with hydrochloric acid and allowed to cool, the acid separated out in fine needles.

From the barium salt, acidified with hydrochloric acid and allowed to stand in a cool place for several days, the acid separated out in large clear prismatic crystals, which appear to belong to the monoclinic system.

Mr. Noyes also states that the acid, when heated rapidly, melts at 105° to 107° . When heated slowly it melts at 153 - 155° . He thinks this is due to the fact

(1) Amer. Chem. Jour. 3 - 17.

that the acid is partially converted into benzoic sulphide, for if the acid is kept at that temperature for a short while it becomes a solid, and then melts at 210°C . The substance in the tube, he says, has the intensely sweet taste which is so characteristic of benzoic sulphide.

He obtained pure sulphide by heating a portion of the acid to 180°C , in an air-bath. He thinks this change is due to a loss of water of constitution and not of crystallization, as evidenced by the fact that the salts of the acid are totally distinct from the salts of benzoic sulphide.

PREPARATION OF ORTHO SULPHUMINE BENZOIC ACID.

Purification of Benzoic Sulphimide.

It occurred to Professor Remsen that the acid could be prepared by boiling pure benzoic sulphide with sodium hydroxide. The benzoic sulphide was purified by the (1) method suggested by Pope, which consists in treating the sulphide with acetone. The sulphide is more soluble in hot than in cold acetone. The para-sulphumine benzoic acid, which is sometimes found in benzoic sulphide as an

(1) Jour. Chem. Society - 6 - 935.

impurity, is insoluble in acetone. This being the case, it is an easy matter to separate the two substances. The sulphinide used in the following experiments contained scarcely a trace of para sulphanine benzoic acid, even before it was treated with ~~ether~~ acetone. One hundred grams of the sulphinide required about 460 grams of acetone.

When the benzoic sulphinide is dissolved in hot acetone a white crystalline mass is deposited immediately upon cooling, but if the sulphinide is dissolved in cold acetone and the solution is allowed to evaporate spontaneously massive, colorless rhombohedrons are deposited, some of which are several millimeters in length.

Hydrolysis of Benzoic Sulphinide.

After a number of experiments it was found that when the benzoic sulphinide is treated with sodium hydroxide, under the following conditions, the orthosulphanine benzoic acid was produced in nearly a quantitative yield: Twenty grams of pure benzoic sulphinide was added to a caustic soda solution, which was prepared by dissolving fifteen grams of sodium hydroxide in five hundred c.c. of water. This solution was evaporated on a water-bath until the sweet taste of the sulphinide could no longer be detected. Now



The solution was allowed to cool and then filtered. The acid was precipitated by means of hydrochloric acid. If the solution is stirred vigorously, after the addition of hydrochloric acid, the acid is precipitated at once as a mass composed of fine crystals. If allowed to stand over night without disturbance large monoclinic crystals are deposited. After filtering, the acid was dissolved in alcohol from which solution it crystallized in large transparent rhombohedrons.

The acid when heated slowly melted at 152°C ; when heated rapidly it melted at 159°C . (uncorrected). It is quite soluble in alcohol and water. Some of the acid was placed in a small boat which was placed in a glass tube with a diameter of about 15 m.m. One end of the tube was connected with a bottle containing a small quantity of sulphuric acid. The other end was connected with a cylinder which contained calcium chloride. By connecting this apparatus with a filter pump, a current of dry air could be drawn through the tube. If a current of air flowing quite rapidly was allowed to pass through the tube, the acid was decomposed when heated to about 128°C . A white sublimate, which was very sweet, collected on the wall of the tube. If the current of air was shut off, the acid decomposed at

135°, and white transparent needles of pure benzoic sulphinide collected on the wall of the tube. Some of the needles were from ~~ten~~¹⁰ to ~~twelve~~¹⁵ m.m. in length. The acid contains no water of crystallization.

The acid crystallizes in white opaque needles if the solution is allowed to stand at least one week before crystallization takes place. The needles melted at 152°. The needles are more soluble in water than the plates. The needle acid contains water of crystallization. Below 110° it lost just one-half a molecule of water.

Calculated for	Found
COOH	
C ₆ H ₅ - 1/2 H ₂ O	I.
~ So CH ₃	4.28
H ₂ O + 2	

The needles when dissolved in alcohol crystallize from the solution in plates which melt at 152°.

The needles decomposed when heated to about 115°; a white sublimate collected on the walls of the tube. The sublimate was very sweet. Ten grams of benzoic sulphinide was added to a caustic soda solution which was prepared by dissolving twenty grams of caustic soda in 250 c.c. of water. The solution was treated in the same way as the previous solution. After treating the solution with hydrochloric

acid if it is allowed to stand over night the acid crystallizes out in the form of needles. These proportions give nearly a quantitative yield of the needle acid.

A careful examination of the needles showed that they agreed in every respect with the needles obtained by the recrystallization of the plate acid from water. Melting point 152°; if the temperature is kept at 152° for a while the acid becomes a solid which melts at 215°. If heated in the apparatus previously described the needles lose one-half molecule of water of crystallization below 100°c.

I - 0.3484 gram of acid lost 0.0150 gram of water at 90°.

II. 0.2930 gram of acid lost 0.0119 gram of water at 98°.

Calculated for	Found.
COOH	I. II.
$C_6H_4 \sim CO_2H_2$	4.30 4.11
H ₂ O 4.24	

If a current of air was allowed to flow rapidly through the tube, the acid decomposed at 115°c. and was partially fused. When the current of air was cut off en-

tirely, the acid decomposed at 145° . This acid was heated at this temperature for about six hours. During this time beautiful transparent needles of pure benzoic sulphinate, some of which were several millimeters in length, collected on the walls of the tubes. The needles were extremely sweet and melted at 23° to 24° (uncorrected). By taking proportions intermediate between the preparations used in the previous experiment (fifteen grams of sodium hydroxide with the same amount of benzoic sulphine&acid water) a yield is obtained which consists partly of the plate acid and partly of the needle acid. On account of the difference in solubility they can be easily separated, the plates being less soluble than the needles.

20 grams of Benzoic sulphinate were added to a caustic soda solution which was prepared by dissolving 20 grams of sodium hydroxide in 750^{c.c.} water. The solution was treated in the same way as in the previous experiments. From 15 to 20 grams of acid were obtained. The solution was set aside. After standing for a week or two, large transparent, monoclinic plates were deposited, which were fairly soluble in water. The crystals after being dried became translucent. Upon examination the substance was found to be a sodium salt, which, upon analysis, gave the

following result:

I. 0.1372 gram of the salt gave 0.0347 gram of Na_2SO_4
II. 0.180 gram of the salt gave 0.0445 gram of Na_2SO_4
III. 0.1084 gram of the salt gave 0.0266 gram of Na_2SO_4

Calculated for

Found

Na

I. II. III.

8.16 7.98 7.93

No loss in weight when heated to 165° , neither did it become sweet.

10 grams of benzoic sulphinide were added to a caustic potash solution which was prepared by dissolving 15 grams of potassium hydroxide in 250 c.c. of water. The solution was treated in the same manner as the previous solutions. After treating the solution with hydrochloric acid it was allowed to stand for several days. During this time large monoclinic plates were deposited. The plates became transparent when dried. Upon examination the substance turned out to be a potassium salt which, upon analysis, gave the following results:

I. 0.2149 gram of salt gave 0.0739 gram of K_2SO_4 ,
II. 0.1478 gram of salt gave 0.0502 gram of K_2SO_4 .

Calculated for	Found
K	I. II.
	15.40 15.42

No loss in weight when heated to 160°.

20 grams of benzoic sulphinide were added to a caustic soda solution which was prepared by dissolving 30 grams of sodium hydroxide in 500c.c. of water. The solution was treated in the same manner as the other solutions, with the exception of placing the beaker in cold water when the hydrochloric acid was added. When the acid was added to the solution quite a considerable quantity of heat was evolved. After cooling, a crystalline mass was deposited. This mass when crystallized from water separated as transparent, monoclinic plates which remained transparent after being dried. The substance turned out to be the acid a monium salt of orthosulphobenzoic acid as evidenced by the fact that ammonia could be detected when the salt was treated with a solution of sodium hydroxide in the cold. Also by the following analysis:

Calculated for		Found.	
COOH		I.	II.
C_6H_5			
SO_3NH_2		35.74	35.79
C -	38.35	4.01	4.35
H	4.10	4.65	
N	1.39		

The salt was converted into potassium salt which was analysed:

K	16.25	16.36
---	-------	-------

Salts of Ortho-Sulphaminebenzoic Acid.

All of the salts crystallize from a water solution, in well formed crystals. All of them contain water of crystallization with the exception of the mono silver, potassium and ~~carbon~~ salts. Without exception they all become sweet when they lose their water of crystallization; indeed they begin to get sweet just as soon as they begin to lose their water.

All the salts decompose at a few degrees above the temperature at which they give off their water of crystallization.

Sodium Ortho-sulphaminebenzoate -

C_6H_5COONa This salt was prepared by treating a hot SO_3NH_2

solution of the acid with pure sodium carbonate to the point of neutralization. The salt crystallizes from an exceedingly concentrated water solution in fine silky needles. Only a few needles were obtained from a solution which was allowed to stand several weeks, in a small test tube. Even then a slight disturbance of the tube would cause the needles to redissolve. As a general rule the salt is deposited as a white amorphous mass. The salt becomes sweet by simply exposing it to the air for a short while. The salt was dried (with dryint paper) and analysed at once. The percentage of sodium agreed with $1\frac{1}{2}$ molecules of water, and the percentage of water of crystallization agreed with $2\frac{1}{2}$ molecules of water.

I. 0.2114 gram of salt lost 0.0357 gram of water below 110° .

II. 0.2210 gram of salt lost 0.0375 gram of water below 110° .

III. 0.2629 gram of salt lost 0.0442 gram of water below 110° .

Calculated for	Found
COONa	
$C_6H_{11}SO_3Na + 1/2 H_2O$	I. II. III.
H_2O 16.79	15.18 16.96 16.71

Calculated for

Found

	COONa	I.	II	III
C_6H_4	+ 1 1/2 H ₂ O			
SO ₂ NH ₂		9.10	9.12	9.11

Na 9.30

A few of the needles were obtained and an analysis of the sodium agreed with 2 1/2 molecules of water.

I. 0.0174 grams of salt gave 0.0046 grams of Na_2SO_4 .

II. 0.1945 grams of salt gave 0.0546 grams of Na_2SO_4 .

Calculated for

Found

	COONa	I.	II.
C_6H_4	+ 2 1/2 H ₂ O		
SO ₂ NH ₂		8.62	8.59

Na 9.59

Potassium Orthosulphaphinebenzoate.

COOK

This salt was prepared by neutralizing the acid with pure potassium carbonate. The salt is extremely soluble in water; insoluble in ethyl alcohol. The salt is deposited from a water solution as a white amorphous mass. It crystallizes from a mixture of alcohol and water in large transparent plates.

I. 0.144 gram of salt gave 0.0536 gram of K_2SO_4 .
 II. 0.129 gram of salt gave 0.0457 gram of K_2SO_4 .

Calculated for	Found	
COOK	I. II.	
$\text{C}_6\text{H}_5\text{NH}_2\text{SO}_4\text{H}_2\text{O}$	16.73 16.20	
K 16.32		

Calcium Orthosulphagine benzoate.

$\text{COO} \left(\text{C}_6\text{H}_5\text{NH}_2 \text{SO}_4\text{H}_2\text{O} \right)_2 \text{Ca} + 2\text{H}_2\text{O}$. A hot solution of the acid is neutralized with pure calcium carbonate. The salt crystallized from a water solution in well formed translucent crystals.

If crystallization takes place at once well formed crystals are obtained; but if the solution is allowed to stand several days, the salt is deposited as a white crystalline mass.

I. 0.1471 gram of salt lost 0.0414 gram of water below 140° .
 II. 0.2776 gram of salt lost 0.0177 gram of water below 140° .

I. 0.2114 gram of salt gave 0.0098 gram of CaCO_3 .
 II. 0.2926 gram of salt gave 0.0139 gram of CaCO_3 .

Calculated for		Found	
$\text{C}_{10}\text{H}_7\text{O}_4$	$\text{C}_6 = 77.0$	I	II
SO_3NH_2		7.17	7.30
Ca	5.40	7.06	7.33
H_2O	7.53		

Barium Orthosulphamino Benzoate -

$\text{C}_{10}\text{H}_7\text{O}_4\text{SO}_3\text{NH}_2 \cdot 3\text{H}_2\text{O}$ - This salt was prepared by treating the acid with pure barium carbonate. It is quite soluble in water and fairly soluble in alcohol. It crystallizes from a water solution in transparent plates, and sometimes it crystallizes from a water solution in needles in the form of rosettes. It crystallizes in needles from alcohol solution. Indications observed in different experiments, point to the conclusion that the salt crystallizes, under different conditions, with a different number of molecules of water of crystallization. It agrees in every respect with the salt prepared by Mr. W. A. Noyes with the exception of the number of molecules of water of crystallization. Mr. Noyes prepared two salts, one with 2 molecules and another one with 3 molecules of water of crystallization. This salt loses its water of crystallization when

(1)

ANALYST, A. C. G. T. 1907, 33, 11.

0.1807 gram of the salt lost 0.0171 gram of H₂O below 150°.

I. 0.1214 gram of salt gave 0.0493 gram of Ba SO₄.

II. 0.1076 gram of salt gave 0.0426 gram of Ba SO₄.

Calculated for		Found	
(C ₆ H ₅ COO) ₂ Pa + 3 H ₂ O		I	II
Ba	23.18	23.39	23.32
H ₂ O	9.14	9.14	

exposed to the air.

Strontium Ortho-sulphaminebenzoate -

$$\left(\text{C}_6\text{H}_5\text{NH}_2 \right) \text{COO} \cdot \text{H}_2\text{O}$$
. This salt is prepared by neutralizing a hot solution of the acid with pure strontium carbonate. If the solution is allowed to evaporate spontaneously the salt crystallizes in long transparent needle-like crystals, some of which are three or four millimeters in length. The crystals remain transparent when exposed to the air.

I. 0.2151 gram of salt lost 0.0150 gram of H_2O below 140°.

I. 0.1365 gram of salt gave 0.0486 gram of Sr SO_4 .

II. 0.2231 gram of salt gave 0.0783 gram of Sr SO_4 .

Calculated for	Found
$\left(\text{C}_6\text{H}_5\text{NH}_2 \right) \text{COO} \cdot \text{H}_2\text{O}$.	I II
	16.71 16.67
Sr. 16.71	16.97
H_2O 0.37	

Zinc Ortho-sulphaminebenzoate -

$$\left(\text{C}_6\text{H}_5\text{NH}_2 \right) \text{COO} \cdot \text{Zn} \cdot \text{ZnO}$$
. Two grams of the acid was dis-

solved in a sufficient quantity of water and pure zinc carbonate was added till the solution was neutral. The solution was evaporated to a slight extent, and allowed to stand in a desicator over night. Short opaque needle-like crystals were deposited during the night. If the solution is allowed to evaporate spontaneously, after several days, large transparent needle-like crystals are deposited, some of which were from one to two centimeters in length. The crystals do not lose their transparency when exposed to the air. The salt is fairly soluble in water.

I. 0.0309 gram of the salt lost 0.0081 gram of water below 130°.

II. 0.0690 gram of salt lost 0.0070 gram of water below 130°.

I. 0.0449 gram of salt gave 0.0137 gram of $Zn SO_4$.

II. 0.0621 gram of salt gave 0.0192 gram of $Zn SO_4$.

III. 0.1476 gram of salt gave 0.0436 gram of $Zn SO_4$.

Calculated for

Found.

	Calcd.	I	II	III
$(C_6H_5)_2SO_4$	600.0	12.34	12.40	12.46
Zn	12.56	10.01	10.17	
H_2O	10.30			

Zinc Ortho-sulphamino benzoate. -

$\text{C}_6\text{H}_4\text{N}(\text{SO}_3\text{NH}_2)_2\text{COO}$ $\text{Zn} + 3\text{H}_2\text{O}$. This salt was prepared from the needle acid in order to compare it with the zinc salt prepared from the plate acid. The two salts resemble one another in every respect with one exception. The solution of this salt, when allowed to evaporate spontaneously deposited large opaque needle-like crystals instead of transparent needles as is the case with the salt prepared from the plate acid.

I. 0.0652 gram of salt gave 0.0201 gram of ZnSO_4 .

I. 0.0138 gram of salt lost 0.0138 gram of water below 150° .

Calculated for		Found
$\text{C}_6\text{H}_4\text{N}(\text{SO}_3\text{NH}_2)_2\text{COO}$	$\text{Zn} + 3\text{H}_2\text{O}$	I.
Zn	12.59	12.42
H_2O	10.39	10.64

Magnesium Ortho-sulphamino benzoate -

$\text{C}_6\text{H}_4\text{N}(\text{SO}_3\text{NH}_2)_2\text{COO}$ $\text{Mg} + \text{H}_2\text{O}$. - This salt was prepared by treating the acid with magnesium hydroxide. The salt

crystallized in well formed transparent needles which are deposited in the form of rosettes. The salt is extremely soluble in water.

I. 0.1850 gram of salt lost 0.0270 below 175°.

II. 0.2458 gram of salt lost 0.0355 gram of water below 175°.

I. 0.2129 gram of salt gave 0.0519 gram of $Mg\text{SO}_4$.

II. 0.1726 gram of salt gave 0.0425 gram of $Mg\text{SO}_4$.

III. 0.1416 gram of salt gave 0.0341 gram of $Mg\text{SO}_4$.

Calculated for

Found

$(C_6H_5COO)_2Cu + 4H_2O$	I.	II.	III.
	4.84	4.92	4.81
Mg 4.84 H_2O 14.52		14.59	14.42

Copper-Ortho-sulphamine-benzoate

$(C_6H_5COO)_2Cu + 3H_2O$. - This salt was prepared by boiling a solution of the acid with freshly precipitated copper oxide, in a sand-bath, for about forty minutes. There was deposited after standing over night, large blue feathery needles, some of which were more than a centimeter in length. The salt is insoluble in alcohol and very diffi-

icultly soluble in water. The salt turned a deep green color when it lost its water of crystallization.

I. 0.1369 gram of the salt lost 0.0144 gram of water below 170°.

II. 0.0195 gram of salt lost 0.0095 gram of water below 170°.

III. 0.0951 gram of salt lost 0.0085 gram of water below 170°.

I. 0.1684 gram of salt gave 0.0209 gram of Cu O.

II. 0.3012 gram of salt gave 0.0456 gram of Cu O.

Calculated for	Found
$\left(\text{C}_6\text{H}_5\text{COO} \right) \text{Cu} + 3\text{H}_2\text{O}$	I II
Cu 12.41	12.41 12.32
H O 10.52	10.52 10.91
H O 10/44	

Mono Silver Ortho-sulphaphine benzoate. —

This salt was prepared by neutralizing two grams of acid with ammonium hydroxide, and then boiling the solution until no odor of ammonia could be detected. Silver nitrate was added to the solution until no further precipitation

to place. By allowing the solution to stand over night there were deposited, fine feathery needles of a light gray color. The salt is soluble in hot water but insoluble in cold water. Becomes dark ~~colored~~ when exposed to the light.

Although it contains no water of crystallization it becomes sweet when heated up to 150°, and changes its color to light brown.

This salt resembles in every respect the salt prepared by Mr. Noyes (1) by the same method.

I. 0.0875 gram of salt gave 0.0307 gram of Ag.

II. 0.1171 gram of salt gave 0.0412 gram of Ag.

Calculated for	Found	
COOAg	I	II
$C_6H_4\backslash SO_3H$	35.08	35.17
Ag 35.06		

Li-Silver Ortho-Eulphamine Benzoate,

$C_6H_4\backslash SO_3H + H_2O$. - This salt was prepared by neutralizing about two grams of acid with ammonium hydroxide and then adding about 3/4 as much ammonium hydroxide in excess as was required to neutralize the solution. Silver nitrate

was boiled until no further precipitation took place. The salt was deposited as a white amorphous mass which was dissolved in boiling hot water. By allowing the solution to stand over night the salt separated out as silver-colored leaflets which became dark colored when exposed to the light. This salt is much less soluble in water than the mono silver salt, and resembles in every respect, with (1) one exception, the di-silver salt prepared by Noyes by treating the barium salt with silver nitrate. This salt contains one molecule of water of crystallization.

The salt was thoroughly dried and was allowed to remain wrapped in drying-paper for about one week. It was then heated to 140° in the apparatus previously described. The current of air was cut off, and water could be distinctly seen as it collected in drops in both ends of the tube. After losing its water it becomes a dark brown color.

I. 0.1231 gram of the salt lost 0.0053 gram of water at 167°.

I. 0.1967 gram of salt gave 0.0933 gram of Ag.

II. 0.1097 gram of salt gave 0.0549 gram of Ag.

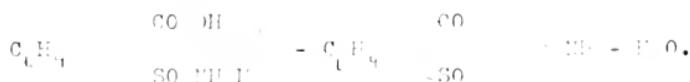
(1) Loc. cit.

Calcd. (%) for		Found	
COO Ar		I	II
$C_6H_5\backslash SO_2NH_2$	+ H ₂ O	49.97	50.04
Ar		49.18	
H ₂ O		4.15	

Ammonium ortho-sulphamino benzoate,

$C_6H_5\backslash SO_2NH_4$ + CO_2 — This was prepared by neutralizing the acid with ammonium hydroxide. The salt is quite soluble in water, and crystallizes from a water solution in transparent plates.

The salt contains no water of crystallization, but becomes very sweet when heated to 125°, and decomposes quite easily. Ammonium ortho-sulphamino benzoate
 Five grams of the acid were mixed with five grams of phosphorus oxychloride and heated on a water-bath for two hours. No chloride was formed. All of the acid was converted into benzoic sulphimide.



This reaction is evidence in favor of the formula given to

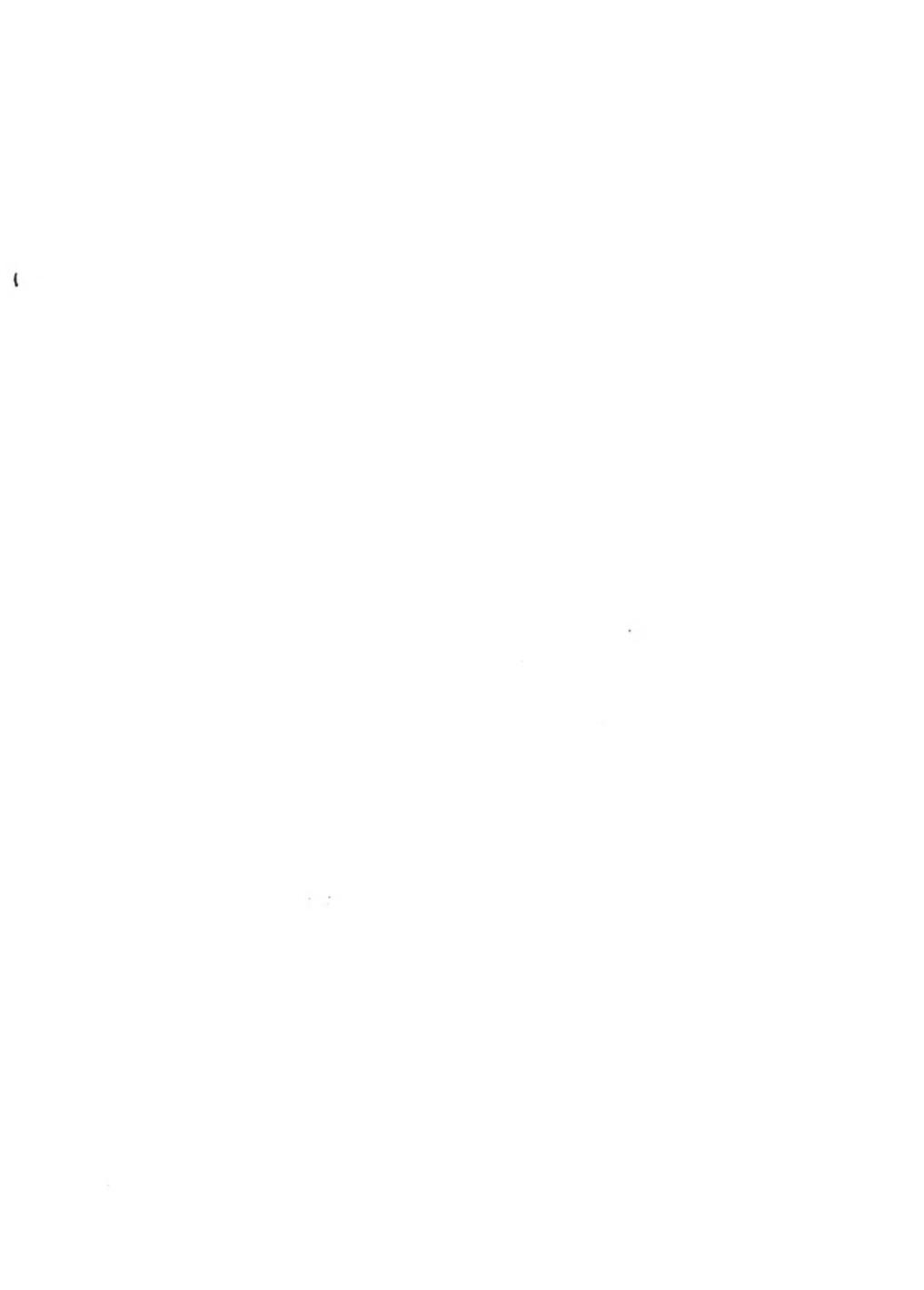
present in Mr. Noyes. In order to prove the presence of this group in the acid, the hydroxyl group of the normal form was destroyed with one drop concentrated sulfuric acid, and the sulfide group was determined by the above formula.

Preparation of the Diamide,

$\text{C}_6\text{H}_5\text{COOH}$ 20 ml., the diamide was prepared by the following method:

Ten grams of the acid were mixed with six grams of potassium cyanate. The mixture was heated, in a closed bath, for three days. During this time it was frequently stirred. As the acid is converted into benzoic sulphinide at quite a low temperature, the mixture was heated from 60° to 100° the first day, from 120° to 135° the second day and from 110° to 150° the third day. The mass, which is of a light straw color, is allowed to cool when it becomes brittle. It is then pulverized and treated with boiling alcohol in which it is soluble. After filtering, the solution is allowed to cool when there is deposited light colored needles. Melting-point 167°.





Analysis of the diamide gave the following results:

I. 0.1296 gram of diamide gave 0.1525 gram of Pb SO_4 .

I. 0.1565 gram of the diamide gave 0.0309 gram of nitrogen.

II. 0.1413 gram of the diamide gave 0.0128 gram of nitrogen.

Calculated for	Found	
$\text{C}_4\text{H}_7\text{NO}_2 \cdot \text{SO}_4\text{NH}_3$	I.	II.
C 16.20	16.20	
S 16.00		13.35 13.27
N 14.00		

I am indebted to Mr. C. E. Waters for the nitrogen determinations. Mr. Waters observed ~~that~~ that the ammonia was given off in two different stages. One portion of the ammonia was given off when the sodium hydroxide solution was dilute; after heating sometime the second portion was given off when the solution had become very concentrated. ~~So~~ there must be some difference in the stability of the two amide groups.

Part II.

ORTHOCARBOBENZENESULPHONIC ACID.

Introduction.

(1)

This acid was first prepared by Fahlberg and ^P _{Asper} by the following method: Ortho sulphonbenzoic acid when treated with ammonia, reacts according to this equation:



The ammonium salt when treated with silver nitrate is easily converted into the silver salt. The free acid is obtained by treating the silver salt with sulphuric acid.

They describe the acid as crystallizing in thick prismatic crystals which are easily soluble in water and alcohol, and contain one molecule of water of crystallization. Melting-point 185 to 186° (uncorrected). By melting the acid with potassium hydroxide, ammonia is given off, but when simply heated no ammonia is given off.

(1)

The acid was prepared later by Jepsurun by heating orthocyanobenzene-sulphone-chloride with water or alco-

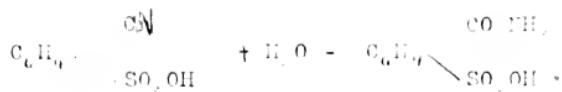
(1) Ber. d. Chem. Ges. 22, 7598

(2) Ber. d. Chem. Ges. 26, 2282.

hol.

(1)

Mr. Karslake also obtained the acid by hydrolysis of ortho-cyanbenzenesulphonic acid by means of dilute alkali:



Preparation of Acid.

The potassium salt of the acid can be obtained in any desired quantity by treating the acid potassium salt of ortho-sulphobenzoic acid with ammonium sulphocyanate⁽²⁾

The acid potassium salt was prepared according to
(3)
the method of Remsen and Saunders.

A modification of the proportions suggested by their method was made for the reason that the benzoic sulphinide used, contained scarcely a trace of para-sulphamino-benzoic acid.

The substances were mixed together in the proportion of five parts of acid potassium salt to three parts of ammonium sulphocyanate. The mixture was heated in a closed

(1) Dissertation, J.H.U., 1896, p.18.
(2) English Patent - Newton & Son - 23, February, 1894.
(3) Dissertation, J.H.U., 1894, p.7.

bath for three days at a temperature from 100° to 200° $\text{F}.$ During this time it was occasionally stirred. The mass which is of a brown color, was allowed to cool when it becomes a stiff cake. It is then finely pulverized and digested with boiling alcohol several times. The potassium salt of the acid which is in the form of sandy crystals was separated from the alcohol by filtering. The salt when recrystallized from water separates out in large transparent plates.

Then the potassium salt is treated with silver nitrate, in the proportion of their molecular weights, reaction takes place with the greatest ease with the formation of the silver salt of ortho $\text{C}_6\text{H}_4\text{SO}_3$ benzene SO_3 acid. The acid is obtained by treating the silver salt with hydrochloric acid. The acid crystallizes from a very concentrated water solution in large, thick, transparent crystals which are quite soluble in alcohol. Melting-point 193° - 194° (uncorrected). The crystals remain transparent when exposed to the air. It does not become sweet when it loses its one molecule of water of crystallization, neither does it become sweet by continued heating. It decomposes when heated to 125° .

I. 0.2691 gram of the acid lost 0.0008 gram of water below 120°.

II. 0.2585 gram of the acid lost 0.0214 gram of water below 120°.

Calculated for	Found	I.	II.
$\text{C}_6\text{H}_5\text{NH}_2 \text{COOH} \cdot \text{H}_2\text{O}$			
	8.47	8.27	
H O	8.22		

Salts of Orthocarbamino_benzenesulphonic acid -

The salts of this acid do not crystallize as well as the salts of orthosulphamino_benzoic acid, but are much more soluble in water.

Most of the salts contain water of crystallization, but none of them become sweet when they lose their water; neither do they become sweet when they are decomposed.

Potassium orthocarbamino_benzenesulphonate ?

$\text{C}_6\text{H}_5\text{NH}_2 \text{COOH} \cdot \text{H}_2\text{O} \cdot \text{K}_2\text{SO}_4$ - This salt was prepared by the method described in the preparation of the acid. It crystallizes from a water solution in large transparent

lates. It is quite soluble in water and alcohol. It crystallizes from alcohol in needles. The salt is eloquent. If the large transparent crystals are placed in a beaker and covered over with water, the moment they become warm a crackling sound can be distinctly heard some distance from the water-bath. The crystals become opaque and crumble to pieces. This phenomenon is doubtless due to the fact that the salt loses its water of crystallization very easily; in this instance loses it under water.

(1) A similar salt is described by Marslake derived (2) from cyanbenzenesulphonic acid, and by Cohen derived from the ammonium salt of benzenesulphonic acid.

I. 0.3439 gram of salt lost 0.0239 gram of water below 100 .

II. 0.5409 gram of salt lost 0.0380 gram of water below 100 .

III. 0.4801 gram of salt lost 0.0331 gram of water below 100 .

I. 0.4460 gram of salt gave 0.1593 gram of Na_2CO_3 .

II. 0.4904 gram of salt gave 0.1657 gram of H_2SO_4 .

III. 0.4216 gram of salt gave 0.1441 gram of H_2SO_4 .

(1) Dissertation, J.H.U., 1895, p.17

" " 1896, p.18

Calculated for		% and		
$\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{CO}_2\text{NH}_2$	H_2O	I.	II.	III.
$\text{C}_6\text{H}_5\text{NH}_2$	CO_2NH_2	15.21	15.11	15.21
N	15.21	14.94	14.91	14.94
H_2O	7.00			

Silver Orthocarbamimebenzene-sulphonate,

$\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{CO}_2\text{NH}_2 \cdot \text{SO}_3\text{Ag}$ + H_2O . — When the potassium salt of the carbamime acid is treated with silver nitrate, in the proportion of their molecular weights, reaction takes place with the greatest ease with the formation of the silver salt. The salt which is fairly soluble in water crystallizes in large monoclinic transparent plates. It is decomposed when brought in contact with wet filter paper, and becomes dark ~~black~~ when exposed to the light for any length of time. The salt is decomposed with the greatest ease when treated with hydrochloric acid or with the chlorides of the metals.

This salt resembles in every respect the salt prepared by Fahlberg and Parme (1) by treating the ammonium salt of the carbamime acid with silver nitrate.

(1) Berichte der D. C. 22, 759.

I. 0.3777 gram of salt lost 0.0193 gram of water below 130°.

II. 0.4146 gram of salt lost 0.0223 gram of water below 130°.

I. 0.3362 gram of salt gave 0.0794 gram of Ag.

II. 0.3681 gram of salt gave 0.1215 gram of Ag.

Calculated for		Found.	
	CO NH	I	II
C_6H_7	$+ H_2O$		
	SO_3OAg	53.19	73.00
Ag	23.14	5.45	5.51
H O	5.52		

Tri-Silver-Ortho-Carbaninebenzenesulphonate 7

C_6H_7 CONAg₃ — A small quantity of the potassium carbaninebenzenesulphonate was dissolved in water, and about two drops of ammonia were added to the solution. A hot solution of silver nitrate was added until no further precipitate was formed. The salt was deposited in a white amorphous mass which was insoluble in boiling water. The salt became dark ~~colored~~ when exposed to the

light and moderately stable. It has the characteristic stability that it does not melt before, the following temperature is reached with indifference.

Calculated for	Found.
CO NH ₂	I
C ₆ H ₅ NH ₂ SO ₃ Na	62.56
Ag	62.07

Sodium Ortho₄carboxyamino₂benzenesulphonate J

CO NH₂
C₆H₅ NH₂ SO₃ Na + CH₃CO. — This salt was prepared by treating the silver salt of sodium carboxyamino benzenesulphonate with silver acetate. It is quite soluble in water, from which ~~saturation~~ it crystallizes in large, transparent plates which belong to the monoclinic system.

This resembles in every respect the salt described (1) by Marslake.

I. 0.1771 gram of the salt lost 0.0214 gram of water below 140°.

II. 0.1870 gram of the salt lost 0.0017 gram of water below 140°.

TABLE III

	COMB	I.	II.
$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{Na}$	$\text{Fe} + \text{H}_2\text{O}$	0.10	0.10
175.0	175.0	175.0	175.0
175.0 - 175.0			

Barium orthocarbonato-nitro-sulfonate step

COMB
 $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{Na}$ } $\text{Fe} + \text{H}_2\text{O}$. - This salt was prepared by treating the silver salt with hydrochloric acid, then adding barium carbonate to the point of neutralization. The salt crystallized in transparent plates from a very concentrated water solution.

The last stage of water of crystallization arises with two molecules of water. The percentage of water agrees with 3 1/2 molecules of water. The following analyses were made of different portions of the salt prepared at different times.

I. 0.1767 gram of salt lost 0.0114 gram of water when
 175.0.

II. 0.2194 gram of salt lost 0.0121 gram of water when
 175.0.

I. 0.017 mmol of salt + 0.037 mmol of SrCO_3 .

II. 0.144 mmol of salt + 0.037 mmol of SrCO_3 .

Calculated for

Found.

$\left(\text{C}_6\text{H}_5\text{CH}_2\text{COO} \right) \text{Sr} + \text{SO}_4\text{O}$ I II
 $\text{C}_6\text{H}_5\text{CH}_2\text{COO}$ 1.37 1.37

SrCO_3 1.37

Calculated for

Found.

$\left(\text{C}_6\text{H}_5\text{CH}_2\text{COO} \right) \text{Sr} + \text{SO}_4\text{O}$ I II
 SO_4O 0.710 0.711

SrCO_3 1.37

—

Strontium Ortho-carbanilidopyromesulphonate r

$\left(\text{C}_6\text{H}_5\text{CH}_2\text{COO} \right) \text{Sr}$ This salt was prepared just as the corresponding ortho-carbanilidopyromesulphonate, strontium orthocarbanilate. The salt separated, out of an extremely concentrated water solution, as small, transparent crystals with no definite form.

I. 0.0148 mmol of the salt + 0.0015 mmol of SrCO_3 .

II. 0.2017 mmol of the salt + 0.0734 mmol of SrCO_3 .

Calculated for

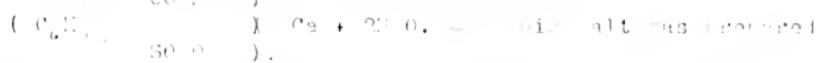
Found.

$\left(\text{C}_6\text{H}_5\text{CH}_2\text{COO} \right) \text{Sr}$

$\left(\text{C}_6\text{H}_5\text{CH}_2\text{COO} \right) \text{Sr}$ 17.00 17.00

SrCO_3 17.00

Calcium Ortho-carbonate and Sulfate 7



by titrating the calcium solution containing salt with a dilute calcium carbonate. The salt precipitated is large transparent calcites from a very concentrated water solution.

I. 0.1333 gram of salt lost 0.0097 gram of water below 186°.

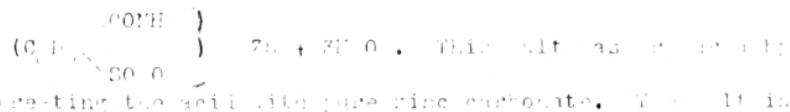
II. 0.1986 gram of salt lost 0.0150 gram of water below 186°.

I. 0.1169 gram of salt gave 0.0322 gram of CaCO_3 .

II. 0.1127 gram of salt gave 0.0323 gram of CaSO_4 .

Calculated for	Found	
$\text{COMH} \quad \left. \begin{array}{l} \text{Ca} \\ \text{CO}_3 \\ \text{SO}_4 \end{array} \right\} \text{Ca} + \text{CO}_3 \text{O}$	I	II
$\text{Ca} \quad 7.16$	7.29	7.25
$\text{CO}_3 \quad 0.40$	0.42	0.47

Zinc Orthocarbonato-sulfate 8



6

isolated from a very concentrated water solution in the form of short ice needles. It is efflorescent.

I. 0.2197 gram of salt lost 0.0117 gram of water below 150°.

II. 0.2477 gram of salt lost 0.0256 gram of H₂O below 150°

I. 0.0934 gram of salt gave 0.0286 gram of ZnSO₄.

II. 0.1010 gram of salt gave 0.0320 gram of ZnSO₄.

Calculated for	Found	
$\text{C}_6\text{H}_5\text{CO}_2\text{H} \quad \text{Zn} + 3\text{H}_2\text{O}$	I	II
(C ₆ H ₅ CO ₂) ₂ + Zn + 3H ₂ O	12.31	12.32
Zn	12.59	10.37
H ₂ O	10.39	10.74

Magnesium*carbaminonaphthalene* sulphonate *

$\text{C}_6\text{H}_5\text{CO}_2\text{H} \quad \text{Mg} + 2\text{H}_2\text{O}$ - This salt was prepared just as the zinc salt by using pure magnesium carbonate. The salt separates out as a crystalline mass from a very concentrated water solution.

I. 0.1983 gram of salt lost 0.0140 gram of water at 140°.

II. 0.2000 gram of salt lost 0.015 gram of water at 140°.

I. 0.1204 gram of salt gave 0.010 gram of K_2SO_4 .

II. 0.1904 gram of salt gave 0.0490 gram of K_2SO_4 .

Calculated for	Found	
$\text{COMg} \left[\begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2 \\ \diagup \\ \text{S} \end{array} \right] \text{SO}_4$	I	II
	5.14	5.14
	7.26	7.19
NH	5.22	
H ₂ O	7.82	

1,4-Di-*tert*-butyl-2,5-dimethyl-3-oxo-4-phenyl-2-pyrrolone

$\left[\begin{array}{c} \text{COMg} \\ \diagup \\ \text{C}_6\text{H}_5\text{CH}_2 \\ \diagup \\ \text{S} \end{array} \right] \text{C}_6\text{H}_5 + 4\text{H}_2\text{O}$. — This salt was prepared by boiling the acid with copper oxide on a water-bath. When allowed to cool, the salt was deposited as beautiful blue plates. When the salt loses its water of crystallization it becomes ~~gray~~. If a small quantity of water is added to the ~~gray~~ salt it becomes light blue ~~yellow~~.

I. 0.1761 gram of salt lost 0.0240 gram of water below 200°.

II. 0.1760 gram of salt lost 0.0240 gram of water below 200°.

I. 0.1083 gram of salt gave 0.0127 gram of CuO.

II. 0.0435 gram of salt gave 0.0064 gram of CuO.

Calculated for		Found	
COMH ₃)	I	I
(C ₆ H ₄ SO ₃) ₂) Cu + 4H ₂ O	11.72	11.72
Cu	11.86	13.62	13.63
H ₂ O	13.45		

Ammonium Ortho-Carbamino-Benzene-Sulphonate

COMH₃
C₆H₄SO₃ONH₄ This salt was prepared by neutralizing the acid with ammonium hydroxide. It crystallized from a concentrated water solution in large plates. One plate obtained was at least 2 1/2 c.c. in length. It gives off ammonia when treated with sodium hydroxide in the cold. After heating the salt up to 140° no sweet taste could be

detected. Melts at 262° to 263° (uncorrected). If the current of ir was cut off water collected in the cold end of the tube when the salt was heated to 125°.

I. 0.1503 gram of salt lost 0.0062 gram of water below 125°.

II. 0.1404 gram of salt lost 0.0059 gram of water below 125°.

I. 0.1562 gram of salt gave 0.1649 gram of Ba SO_4 .

Calculated for	Found		
COMH_2		I.	II
$\text{C}_6\text{H}_{14}\text{N}_2 \cdot \text{SO}_4 \text{ONH}_4 + 1/2 \text{H}_2\text{O}$	4.12	4.20	
H_2O 3.96			

Calculated for	Found	
COMH_2	I	
$\text{C}_6\text{H}_{14}\text{N}_2 \cdot \text{SO}_4 \text{ONH}_4$	14.46	
S. 14.67	(1)	

This salt was prepared by Fahlberg and Parme in. Described as crystallizing from alcohol in white needles which melt at 125° - 225°. Jepsturun describes it as crystal-

(1) Loc. cit. (2) Loc. cit. (3) Loc. cit.

lizing from water in transparent crystals containing one molecule of water of crystallization. Karslake describes the salt as crystallizing from a water solution, in transparent rods, which contain no water of crystallization and which melted at $219^{\circ} - 220^{\circ}$ (uncorrected).

Preparation of Chloride.

Five grams of the potassium salt was mixed with five grams of phosphorus oxychloride in a small flask. The flask was attached to a return condenser, and then placed in a bath which contained boiling water. The mixture was heated for about one-half an hour. The white mass was pulverized in a mortar and treated with cold water, the orthocarbanine-benzene-sulphone-chloride, which remains in the form of white crystalline powder insoluble in water is filtered off. It was then thoroughly dried. It crystallized from chloroform solution in small thick opaque plates.

Melting-point 63°.



I. 0.1106 gram of salt gave 0.0934 gram of AgCl (Carrie method).

(1) Loc. cit.

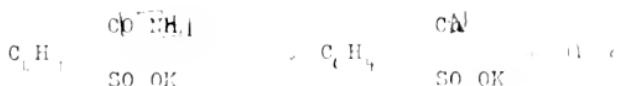
Calcd. for	Found
COOH	
C ₆ H ₅	I.
SO ₃ Cl	13.00
Cl	16.17

Potassium Orthocyanbenzenesulphonate

CN

C₆H₅ SO₃OK . . . This salt was prepared by treating the potassium salt with phosphorus oxychloride as in the previous experiment, only the mixture in this experiment was simply warmed in the water-bath. The whole of the potassium salt was converted into the cyan salt. It crystallizes from a moderately dilute water solution in small transparent needles radiating from a common centre.

If the mixture of the potassium salt and phosphorus oxychloride is placed in a cold water bath, and then heated to the boiling temperature, the potassium salt will be partly converted into the chloride and partly into the cyan potassium salt.



This reaction is evidence in favor of the formula given to the acid by Fahlberg and Barge.¹

This salt resembles in every respect the salt described
(1) by Moyes, derived from ammonium cyanbenzenesulphonate.

Calculated for

Found.

	CN	I	II
C_6H_5	So. OK		
K	17.67	17.17	17.71

A small portion of the chloride was placed in a beaker which was then placed in a dish of cold water. The chloride was treated with a small quantity of an ordinary solution of ammonium hydroxide. The beaker was allowed to stand in the water for about three hours, being stirred at frequent intervals. It was then warmed on a water-bath for about half an hour. The solution was then filtered and a white crystalline substance remained on the filter paper. It was soluble only in boiling alcohol from which solution it crystallized in small opaque monoclinic (?) plates. The substance did not melt when heated to the boiling-point of sulphuric acid. A sulphur determination was made by the Liebig method. Ammonia was given off when the substance was fused with potassium hydroxide, although not as freely as in the case of the sulphamine diamide. This substance seemed to be more stable than the sulphamine diamide.

I. 0.1203 gram of substance gave 0.1506 mm. of BaSO_4 .

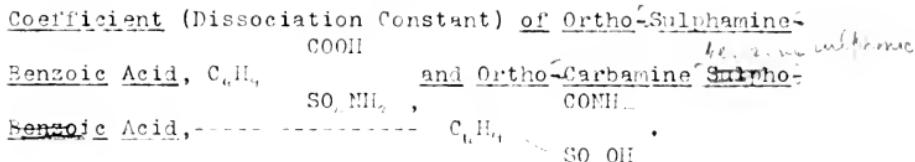
Calculated for	Found
$\text{CO} \cdot \text{NH}_2$	I
$\text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{SO}_3 \cdot \text{NH}_2$	
S. 16	17.20

Possibly the substance was not thoroughly oxidized when fused with potassium hydroxide or else it is not the carbamine diamide.

Appendix.

The following work was done by Mr. Benjamin Palmer Caldwell, a student in the department of Physical Chemistry -

Determination of the Molecular Conductivity and Activity Coefficient (Dissociation Constant) of Ortho-Sulphamino-



The conductivity was determined by the method of Kohlrausch (Zeit. phys. Chem., I, 105; 2, 902) using a Wheatstone bridge, induction coil, and telephone.

Since organic acids, in general, are not strongly dissociated in solution, complete dissociation is only reached at dilutions far too great to permit the use of the conductivity method. The conductivity of the sodium salt at infinite dilution is, therefore, ~~obtained~~, since this is strongly dissociated, and that of the acid is computed from this value by subtracting the constant for the Sodium ion, 49, and adding to the remainder the constant for the Hydrogen ion, 325. In the case of the Ortho-sulphamino-Benzoic acid, this was not done, since the composition of the try

sodium salt was not positively ascertained. The value 360, was taken as the molecular conductivity of the acid at complete dissociation, it having been seen in the examination of the results of Ostwald's work on organic acids (Zeit. Phys. Chem. 3, 170, 240, 300.) that the value for a very large number of closely related monobasic acids fell between 317 and 362. This number, for monobasic acids is the sum of the hydrogen constant, 325, and the constant for the cation made up of the rest of the acid. This latter constant is nearly the same throughout, for a large number of acids. The value, 360, cannot be wrong by more than two units - ~~analytically~~ which would not ~~necessarily~~ affect the results dependent upon it ~~analytically~~.

Normal dilution

In the case of the Ortho-carbamino ~~Sulpho~~ ^{Ammonium} Benzoic acid, the sodium salt was employed, and the value for the molecular conductivity of that acid at complete dissociation was computed as shown above.

The amount of dissociation at any specified dilution, α , is obtained by dividing the molecular conductivity at that dilution κ_{α} by the molecular conductivity at infinite dilution κ_{∞} - that is, at complete dissociation: $\alpha = \frac{\kappa_{\alpha}}{\kappa_{\infty}}$

The chemical activity of acids is directly propor-

tional to the dissociation constant, k . This is obtained by the formula of Ostwald (Zeit. Phys. Chem., 3, 172), which was deduced from the condition of a dissociating vapor

$$A = \frac{C^2}{C + K} \cdot \frac{1}{V}$$

Where V is the number of litres of solution containing a gram molecule of the dissolved substance. This formula holds for weakly dissociated substances, but fails when applied to strongly dissociated compounds.

The results obtained by Mr. Caldwell are given below with the acids, submitted to me for examination.

$\text{C}_6\text{H}_5\text{COOH}$		Molec. Wt. 201 146	Temperature 25°
Volume	Conductivity	Dissociation, 100	Dissociation constant, 100 k .
25	75.95	21.09	0.2254
50	101.74	28.23	0.2221
100	133.59	37.19	0.2361
200	171.1	47.65	0.2264
400	212.46	59.02	0.2125
800	251.10	69.07	0.1928
1600	278.12	77.02	-
3200	300.14	83.37	-
6400	323.41	89.83	-

12800 734.21 92. 9 -

$\bar{M}_w = 360$ 100k (mean of first five) 0.224.

I omit the last four values for the dissociation constant. The conductivity of the water at high dilutions brings in a slight error in the molecular conductivity as determined, and slight errors there are often magnified ten times or more in the calculation of dissociation constants.

COMPOUND		Molec. Wt. 259 213. Temperature, 25°
C ₆ H ₅ SO ₃ Na	+ 2H ₂ O	
Volume		Conductivity
20		69.056
40		72.905
80		75.510
160		78.530
320		80.510
640		82.355
1280		85.505
2560		87.140

The error from the water commences to show itself at N/1280 dilution. The correct conductivity for complete dissociation is about 85.

49 + 1% = 50 l. 10% of the acid.

CONC.
 $C_6H_5CO_2H$ + H₂O. Molec. wt. 112-114.
 50.00
 μ = 361. Temperature 25

Volume.	Conductivity,	Dissociation, 100
50	317.01	87.81
100	326.53	90.45
200	331.96	91.95
400	334.55	92.70
600	334.58	92.70
1000	336.12	93.81
1200	344.70	94.48
1400	357.16	95.02
1500	Too dilute to work.	

$$100 \text{ k} = 12.64.$$

The water used in all of the above work was distilled from acid potassium bichromate and alkaline potassium permanganate in the way described by Jones and Mackay in (Am. Chem. Jour., 19, 21). *Zeitsch. Phys. Chem.*, 2, 177.

~~WATER FILTERED.~~

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Biographical.

Francis Daniel Wilson was born in Chatham, Virginia, December 3, 1871. His primary education was received in the public school of that town. After engaging in the mercantile business for three years he entered the Virginia Polytechnic Institute at Blacksburg, Virginia in fall of 1890, and received the degree of Bachelor of Science in 1894, and Master of Science in 1896. During the two years, from 1894 to 1896, he was assistant in General and Analytical Chemistry. In the fall of 1896 he entered the Johns Hopkins as a student in Chemistry, Geology and Mineralogy.

Each year he was appointed to ordinary Virginia scholarships.







